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The specific heat of superheated steam

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THE SPECIFIC HEAT OF SUPERHEATED STEAM

BY

ARTHUR SARIAH GROSSBERG

THESIS FOR THE DEGREE OF BACHELOR OF SCIENCE

IN MECHANICAL ENGINEERING

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Arthur S riah Grossberg

ENTITLED The Specific Heat of Superheated Steam

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DEGREE OF Bachelor of Science in Mechanical Engineering

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THE SPECIFIC HEAT OF SUPERHEATED STEAM

I

HISTORICAL REVIEW.

Although superheated steam finds a very extensive use in the technical world, little has been knows, until very recently, of one of its important physical properties, namely, its specific heat at constant pressure.

Regnault's experiments in 1862, all conducted at atmospheric pressures, and at temperatures relatively close to the saturation limit, did not seem to prove that the specific heat at constant pressure (C_p) is independent of either the pressure or the temperature; still the well known value he derived, $C_p = 0.48$, has been accepted generally for all temperatures and pressures.

Later determinations which have been made show that Cp varies not only with the temperature, but with the pressure as well. The experiments of Mallard and Le Chatelier in 1883, and of Berthelot and Vielle in 1885, made by explosion tests at very high temperatures, indicated that the specific heat (Cp) varied with the temperature. This was corroborated in 1903 by the determinations of Langen, who advanced the formula: $Cp = 0.439 + 0.000239\ t$, (1) where t is the temperature on the C. scale.

In 1905, Holborn and Henning conducted a series of very careful and accurate calorimetric determinations at atmospheric pressures, and at temperatures varying from 100 C. to 820 C.—much lower than those of Langen. These tests lead to the formula:

$Cp = 0.446 + 0.0000856\ t$ (2) This is again a linear relation,

but the coefficient of t is smaller than in Langen's formula. All these experiments indicate that the specific heat (Cp) increases with the temperature, but give no evidence regarding the influence of pressure.

The effect of pressure upon the specific heat (Cp) was first determined by Grindley in 1900. With a throttling calorimeter he throttled saturated steam at pressures of from 14 to 2 atmospheres to produce superheated steam at lower pressures. The result seemed to show that Cp is independent of the pressure and increases with the degree of superheating. This conclusion was so contrary to all accepted theories that other experimental determinations were necessary, and prompted the calorimetric determinations of H. Lorenz in 1905. These showed that in the region of saturation Cp increases with the pressure and decreases with an increasing temperature. R. Linde obtained the same result in his thermodynamic calculation of Cp. It was because the values of Lorenz and Linde differed so widely that Knoblauch and Jacob undertook a very elaborate series of direct determinations of the specific heat at various pressures and temperatures.

These tests, made at the laboratory of technical physics at the Technical High School of Munich during the time from October, 1904, to December 1905, also show conclusively that Cp depends on the pressure as well as on the temperature.

The tests were conducted in the following manner: Steam was passed through a first series of superheaters to remove all traces of moisture. It was then passed through a second, an electrical superheater, in which the heat supplied as electrical energy was

accurately measured. The specific heat was calculated from the ratio of the heat supplied to the rise in temperature. The tests covered a range of temperatures from saturation to 350° C at pressures of 2, 4,6 and 8 atmospheres respectively.

From the results of the tests, the following conclusions were drawn by the experimenters.

1. At constant temperature, C_p increases with increasing pressure.

1 (a) Near saturation, this rate of increase with the pressures increases, while it seems to decrease at high superheats.

2. For a given pressure, C_p falls gradually with increasing temperature, reaches a minimum, and rises again.

2 (a) With increasing pressures, this minimum value appears at higher temperatures.

II

EQUATIONS FOR C_p

Starting with a new form of characteristic equation for superheated steam, Prof. G. A. Goodenough has deduc ed an equation for Cp which gives values that agree substantially with the experimental results of Knoblauch and Jacob.

Writing the characteristic equation in the form

$$v = \frac{BT}{p} - (1 + ap)\frac{m}{T^n}, \quad (3)$$

which is a modified form of Linde's equation, we have by successive differentiation

$$\frac{\partial v}{\partial T} = \frac{B}{p} + \frac{mn}{T^{n+1}}(1 + ap) \quad (4)$$

$$\frac{\partial^2 v}{\partial T^2} = -\frac{mn(n+1)}{T^{n+2}}(1 + ap) \quad (5)$$

Now making use of the well known thermodynamic relation

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -AT\frac{\partial^2 v}{\partial T^2} \quad (6)$$

$$\left(\frac{\partial C_p}{\partial p}\right)_T = \frac{Amn(n+1)}{T^{n+1}}(1 + ap) \quad (7)$$

Taking T as constant, and integrating (7) with p as the independent variable, the result is

$$C_p = \frac{Amn(n+1)}{T^{n+1}} \cdot p\left(1 + \frac{a}{2}p\right) + \text{constant [of integration}$$

Now since T was taken as constant, the constant of integration may be some function of T; hence we may write

$$C_p = \phi(T) + \frac{Amn(n+1)}{T^{n+1}} \cdot p\left(1 + \frac{a}{2}p\right) \quad (8)$$

Inspection of (8) shows that as T is increased, the last term

grows smaller; in fact, Cp approaches ϕ (T) as T is indefinitely increased. Now from Langen's experiments it is seen that at very high temperatures Cp is given by an equation of the form

$$Cp = a + bt$$

hence we are justified in assuming that

$$\phi(T) = \alpha + \beta T$$

where α and β are constants to be determined from experimental evidence. Equation (8) thus becomes

$$C_p = \alpha + \beta T + \frac{Amn(n+1)}{T^{n+1}} \cdot p \left(1 + \frac{a}{2} p\right)$$

This is the general equation for the specific heat of superheated steam at constant pressure.

It may be seen at once that this equation will give values agreeing in a general way with the results of Knoblauch and Jacob. At a given temperature T, the specific heat increases with the pressure. Furthermore, Cp has a minimum value as appears by equating to zero the derivative

$$\frac{\partial C_p}{\partial T} = \beta - \frac{Amn(n+1)^2}{T^{n+2}} p \left(1 + \frac{a}{2} p\right)$$

The following values are given to the constants to make equation (9) fit fairly well to all the experimental results of Knoblauch and Jacob.

$$\alpha = 0.372$$

$\beta = 0.0001$ for the F. Scale

$\beta = 0.00018$ " " C. "

Combining the constants A m n (n+1) into one constant, we have as the final formula for the specific heat,

$$C_p = 0.372 + 0.0001T - p(1 + 0.00035p)\frac{C}{T^{4.5}} \quad (9)$$

where log. C = 9.96790 (Pressure in lb. per sq.in.)

III

SPECIFIC HEAT CURVES

This formula has been used to calculate the values for specific heats at constant pressure (Cp) from saturation to 1000° F. at intervals of every 25° F., and at pressures of 0,1, 3,5, and up to 30 lb. per sq.in. at 5 lb. intervals, and from 100 to 300 lb. at 25lb. intervals. These calculated values of Cp are tabulated in Table I, as are also the saturation temperatures for the pressures used in the calculation. The latter were obtained from Marks and Davis' Steam tables. With the values of Cp from Table I, as ordinates, and temperatures in F. as abscissae, curves of constant pressures were plotted for the values used, and are shown on page (15). Page (12) shows a sample calculation. A short discussion of these curves is thought advisable:

TABLE I. - C_p

CALCULATED VALUES OF SUPERHEATED STEAM AT VARYING PRESSURES AND TEMPERATURES.

Absolute Press. (p)	o	1	3	5	10	15
Saturation Temp. (t_s)	---	101.83	141.5	162.3	193.2	213.0
Temp. °F, $t = t_s$	---	.4321	.4410	.4464	.4574	.4657
t = 100	.42796	----	----	----	----	----
150	.43296	.4357	.4412	----	----	----
200	.43796	.4399	.4437	.4475	.4571	----
225	.44046	.4420	.4450	.4484	.4566	.4648
250	.44296	.4443	.4467	.4496	.4568	.4638
275	.44546	.4465	.4487	.4511	.4571	.4633
300	.44796	.4490	.4510	.4530	.4581	.4632
325	.45046	.4512	.4529	.4549	.4591	.4637
350	.45296	.4536	.4552	.4568	.4604	.4644
375	.45546	.4560	.4573	.4588	.4621	.4652
400	.45796	.4585	.4597	.4608	.4638	.4667
425	.46046	.4608	.4620	.4630	.4656	.4682
450	.46296	.4632	.4643	.4652	.4674	.4697
475	.46546	.4657	.4664	.4674	.4694	.4715
500	.46796	.4683	.4690	.4697	.4715	.4732
525	.47046	.4707	.4713	.4720	.4737	.4752
550	.47296	.4731	.4737	.4743	.4758	.4772
575	.47546	.4756	.4761	.4766	.4779	.4793
600	.47796	.4782	.4786	.4791	.4802	.4814
625	.48046	.4806	.4811	.4816	.4826	.4836
650	.48296	.4831	.4835	.4839	.4849	.4857
675	.48546	.4856	.4860	.4864	.4873	.4880
700	.48796	.4881	.4884	.4887	.4895	.4902
750	.49296	.4931	.4934	.4937	.4943	.4949
800	.49796	.4981	.4983	.4985	.4990	.4995
850	.50296	.5031	.5033	.5035	.5040	.5045
900	.50796	.5080	.5082	.5084	.5087	.5091
950	.51296	.5130	.5132	.5133	.5136	.5140
1000	.51796	.5180	.5181	.5182	.5185	.5188

Abs. Pr. (p)	20	25	30	40	50	60	70	80
Sat. Temp. (t_s)	228.0	240.1	250.3	267.3	281.0	292.7	302.9	312.0
Temp. °F, $t = t_s$	.4725	.4788	.4847	.4946	.5036	.5121	.5198	.5266
t = 100	----	----	----	----	----	----	----	----
150	----	----	----	----	----	----	----	----
200	----	----	----	----	----	----	----	----
225	----	----	----	----	----	----	----	----
250	.4707	.4773	----	----	----	----	----	----
275	.4691	.4751	.4813	.4932	----	----	----	----
300	.4684	.4734	.4786	.4889	.4993	.5100	----	----
325	.4681	.4725	.4770	.4859	.4975	.5041	.5132	.5224
350	.4682	.4721	.4759	.4837	.4915	.4994	.5073	.5153
375	.4687	.4719	.4754	.4821	.4892	.4957	.5027	.5094
400	.4797	.4721	.4755	.4815	.4874	.4935	.4996	.5057
425	.4706	.4731	.4759	.4811	.4864	.4917	.4970	.5024
450	.4720	.4743	.4766	.4812	.4858	.4905	.4953	.5000
475	.4734	.4756	.4776	.4816	.4857	.4899	.4940	.4982
500	.4751	.4769	.4787	.4823	.4859	.4896	.4933	.4970
525	.4767	.4784	.4801	.4932	.4865	.4899	.4931	.4964
550	.4786	.4800	.4815	.4844	.4872	.4902	.4932	.4961
575	.4805	.4819	.4832	.4857	.4883	.4908	.4936	.4963
600	.4825	.4837	.4848	.4871	.4895	.4918	.4942	.4966
625	.4846	.4856	.4865	.4888	.4907	.4929	.4951	.4973
650	.4867	.4876	.4883	.4904	.4923	.4942	.4962	.4981
675	.4887	.4897	.4994	.4923	.4940	.4956	.4974	.4992
700	.4910	.4918	.4925	.4941	.4956	.4972	.4988	.5004
750	.4955	.4961	.4967	.4982	.4996	.5009	.5021	.5034
800	.5001	.5006	.5011	.5022	.5032	.5043	.5054	.5065
850	.5050	.5055	.5059	.5068	.5077	.5086	.5095	.5104
900	.5095	.5098	.5102	.5110	.5117	.5125	.5133	.5140
950	.5143	.5146	.5149	.5156	.5163	.5169	.5175	.5181
1000	.5190	.5193	.5196	.5201	.5207	.5212	.5218	.5224

TABLE I-CONTINUED.

Absolute Press.-p	90	100	125	150	175	200	225
Saturation Temp.-t_s	320.3	327.8	344.4	358.5	370.8	381.9	391.9
Temp. °F, $t = t_s$	.5337	.5397	.5540	.5671	.5785	.5918	.6033
t = 300	----	----	----	----	----	----	----
325	.5317	----	----	----	----	----	----
350	.5234	.5314	.5517	----	----	----	----
375	.5164	.5239	.5410	.5591	.5774	----	----
400	.5118	.5179	.5335	.5496	.5657	.5821	.5988
425	.5078	.5131	.5269	.5410	.5552	.5696	.5842
450	.5047	.5094	.5215	.5340	.5465	.5592	.5722
475	.5025	.5067	.5173	.5283	.5394	.5507	.5621
500	.5008	.5045	.5140	.5238	.5336	.5436	.5538
525	.4997	.5030	.5115	.5202	.5290	.5379	.5469
550	.4991	.5020	.5096	.5174	.5252	.5332	.5412
575	.4989	.5016	.5083	.5153	.5223	.5294	.5366
600	.4990	.5013	.5074	.5137	.5200	.5264	.5329
625	.4994	.5015	.5070	.5126	.5183	.5241	.5299
650	.5001	.5020	.5069	.5120	.5171	.5214	.5276
700	.5020	.5035	.5076	.5118	.5160	.5202	.5246
750	.5046	.5058	.5092	.5127	.5161	.5196	.5232
800	.5076	.5087	.5115	.5144	.5173	.5202	.5232
850	.5107	.5118	.5142	.5167	.5192	.5216	.5241
900	.5148	.5156	.5176	.5196	.5217	.5237	.5259
950	.5188	.5194	.5212	.5230	.5248	.5266	.5283
1000	.5229	.5235	.5249	.5264	.5280	.5294	.5310

Absolute Press.--p	250	300
Saturation Temp.-t_s	401.1	417.5
Temp. °F, $t = t_s$	.6150	.6357
$t = 300$	----	----
325	----	----
350	----	----
375	----	----
400	----	----
425	.5991	.6295
450	.5853	.6121
475	.5737	.5975
500	.5641	.5853
525	.5561	.5749
550	.5495	.5662
575	.5440	.5590
600	.5395	.5530
625	.5354	.5480
650	.5330	.5439
700	.5290	.5380
750	.5269	.5343
800	.5262	.5324
850	.5268	.5318
900	.5280	.5324
950	.5302	.5339
1000	.5325	.5357

Marks and Davis have attempted such a series of curves based on the results of Knoblauch and Jacob. The higher pressures have been extrapolated from Knoblauch's data, while the atmospheric curve has been lowered at high superheats to join continuously with the curve of Holborn and Henning. Again, the curves for pressures below 15 lbs. have been raised at the saturation end because Knoblauch's values run even lower than Regnaults recomputed values at 15 lbs. pressures. A comparison with the curves here presented, shows that those of Marks and Davies are much sharper and rise much faster toward the saturation curve. On the 300 lb. curve the saturation value given by Marks and Davis is 0.89, while from the calculated curve, it attains a value of only 0.63.

The K and J curves are purely empiracal and were made to pass as closely as possible through the experimental points, regardless of the fact that those points might be somewhat in error. As a check on the saturation values, the values of C_p may be calculated from the formula

$$C_p = \frac{dH}{dT} - \frac{r}{T} + \frac{r}{u}\left(\frac{\partial v}{\partial T}\right) \qquad (10)$$

Values of H,r,T and u being taken from Marks and Davis' recent accurate steam tables. This calculation shows the following results:

VALUES OF C_p AT SATURATION

Pressure lbs.per sq.in.	From (10)	From (9)	From K & J Curves
15	0.4727	0.4657	0.47
50	0.4973	0.5038	0.508
100	0.5389	0.5398	0.566
150	0.5705	0.5682	0.630
200	0.6037	0.5928	0.703
300	0.6593	0.6355	0.895

The values given by (10) cannot be far from the truth if the steam tables recently put forth are as accurate as they are assumed to be; hence, it appears that the calculated curves are more nearly correct near the saturation limit than the empirical curves assumed by Knoblauch and Jacob.

SAMPLE CALCULATION FOR (Cp)

Take for example the Cp of superheated steam at a temperature of, say 600 ° F. and at a pressure of 250 lbs. per sq. in.

Formula:-

$$Cp = .372 + 0.0001\,T - p(1 + 0.00035p)\frac{C}{T^{4.5}} \qquad (10)$$

$T = 600 + 459.6 = 1059.6$ $\qquad$ $p = 250$, $\log.p = 2.39794$

$\log.T = 3.02514$ $\qquad$ $\log.(1 + 0.00035p) = 0.03643$

$4.5 \log T = 13.61314$

	2.43437
log C =	9.96790
	12.40227
-4.5 log. T =	13.61314
log. 3rd term =	8.78913-10
3rd term =	0.06154
2nd term = .0001 T	0.10596
1st term =	0.372
Cp = Sum of 3 terms =	0.53950

IV

CURVES OF MEAN SPECIFIC HEAT.

While the values given by Table I are valuable as scientific data, and useful for laboratory investigation, they are not of much practical use in many of the calculations relating to superheated steam. For such a purpose, the mean specific heat for the temperature range involved is more immediately applicable. The mean value of Cp at any pressure between saturation and a definite temperature is the mean ordinate of the curve of that pressure from saturation to the temperature in question. This mean ordinate was found by measuring areas by means of a planimeter. The mean Cp was found for every 50° of temperature from saturation to 1000°. The results are given in Table II, shown on page (15).

As these determinations of the average Cp have all been obtained by a mechanical process, it is very necessary that they be checked mathematically at one or more points on each pressure curve. The formula is very easily deduced from (10) as follows:

$$\text{Mean Cp} = \frac{\int_{T_1}^{T_2} C_p \cdot dT}{T_2 - T_1} \qquad (11)$$

which, by substituting, is:

$$\text{Mean Cp} = \frac{1}{T_2 - T_1}\int_{T_1}^{T_2}\left[\alpha + \beta T + \frac{Amn(n+1)}{T^{n+1}} \cdot p \cdot \left(1 + \frac{a}{2}p\right)\right] \cdot dT = \frac{\left[\alpha T + \frac{\beta}{2}T^2 - \frac{Am(n+1)}{T^n} \cdot p\left(1 + \frac{a}{2}p\right)\right]_{T_1}^{T_2}}{T_2 - T_1} \qquad (12)$$

As this calculation is rather long, the mean Cp at each pressure was checked for only two temperatures, namely: 600° and 1000° F. A sample calculation is shown on page (14).

With the values of the mean Cp from Table II as ordinates and with the temperatures as abscissae, another series of constant pressure curves were plotted and are shown on page (17). This diagram gives a very convenient means of finding a working value for the specific heat of superheated steam at constant pressure for any practical temperature range.

SAMPLE CALCULATION FOR MEAN Cp:

Take for example, the average Cp between saturation and 600 temperature at 250 lb. per sq. in. pressure:

As before

$\alpha = .372 \qquad \beta = 0.0001 \qquad \log. C = 9.96790$

and formula reduces to

$$\frac{\left[0.372\,T + 0.00005\,T^2 + \frac{p(1+0.00035p)}{-3.5}\cdot\frac{C}{T^{4.5}}\right]_{T_1}^{T_2}}{T_2 - T_1}$$

$T_2 = 600 + 459.6 = 1059.6 \qquad T_1 = 401.1 + 459.6 = 860.7$

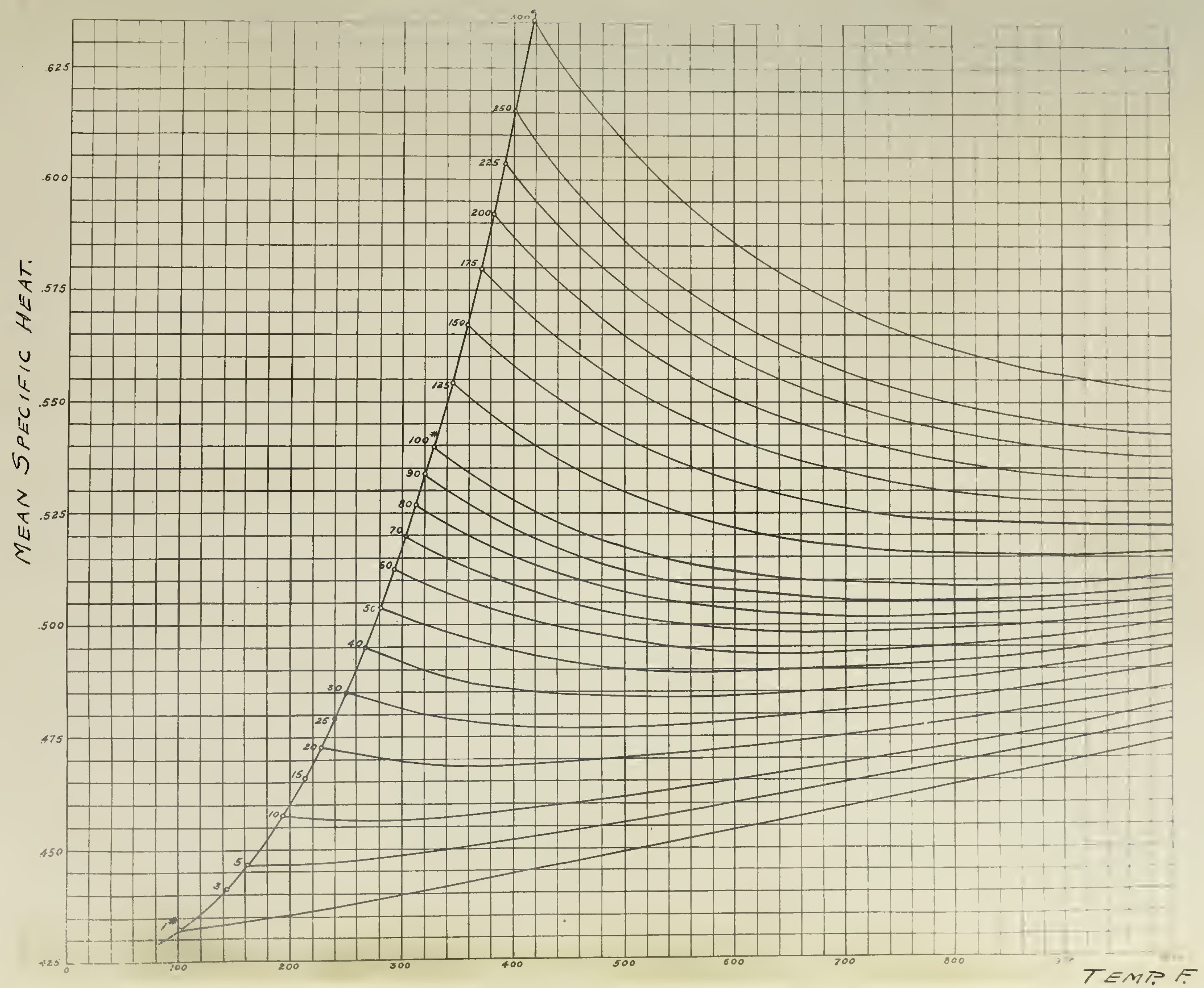
$T_2 - T_1 = 1059.6 - 860.7 = 198.9$

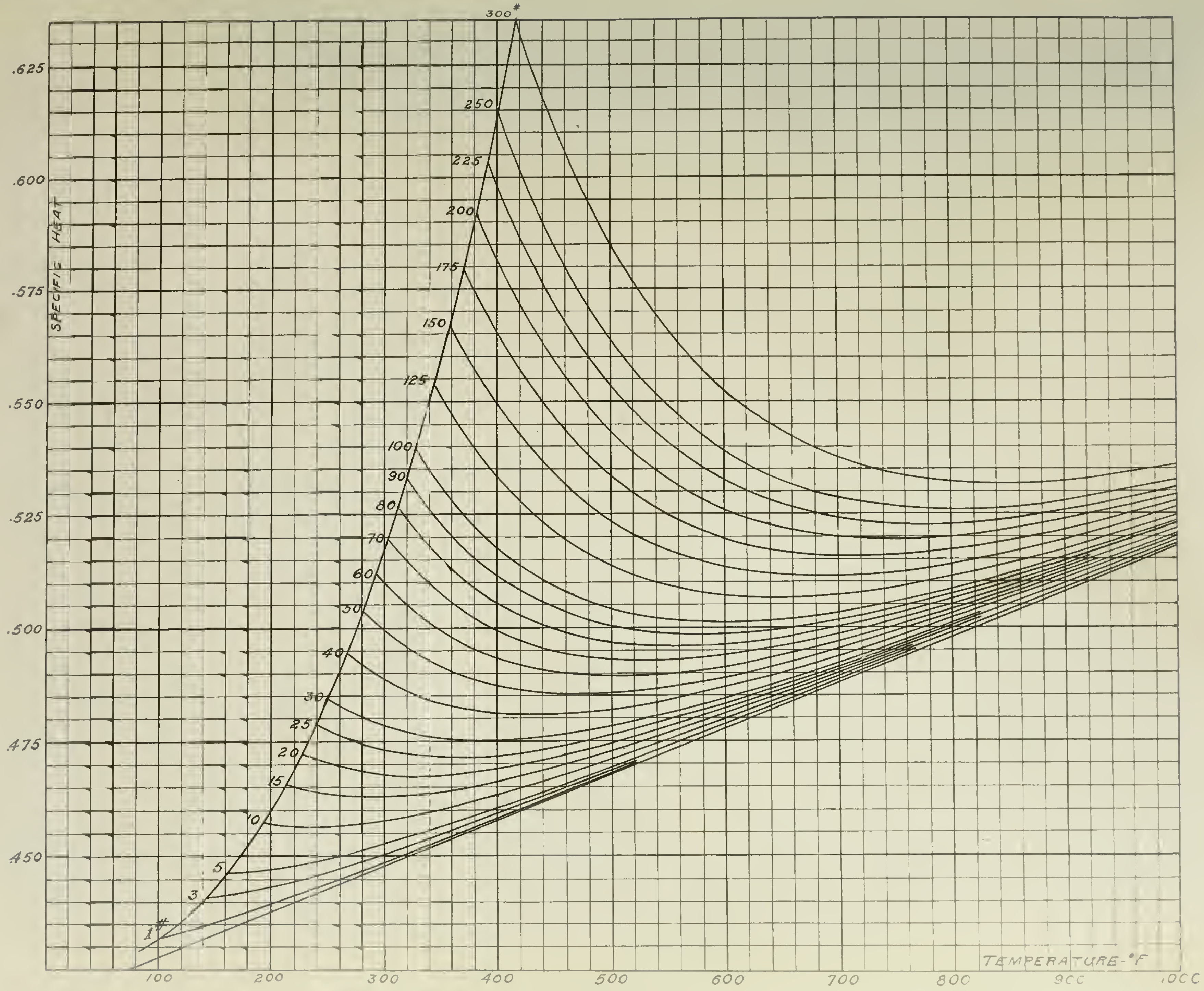
$\log[p\,(1+0.00035p)] = 2.43437$
$\log.C = 9.96790$
12.40227
$\log.3.5 = 0.54407$
11.85820
$3.5 \log. T_2 = 10.58800$
$1.27020 = \log.^{-1} \quad 18.63$

$11.85820 - 3.5 \log.T_1 = 1.58622 = \log.^{-1} \quad 38.57$
19.94

$0.372\,T_2 - 0/372\,T_1 = 394.17 - 320.18 = 73.99$
$0.00005\,T_2^2 - 0.00005\,T_1^2 = 56.14 - 37.04 = 19.10$
113.03

$$\text{Mean Cp} = \frac{113.03}{T - T} = \frac{113.03}{198.9} = 0.5680, \quad \underline{\text{Ans}}.$$


MEAN SPECIFIC HEAT.
TEMP. F.
.425
.450
.475
.500
.525
.550
.575
.600
.625
0
100
200
300
400
500
600
700
800
1
3
5
10
15
20
25
30
40
50
60
70
80
90
100
125
150
175
200
225
250
300



SPECIFIC HEAT
.625
.600
.575
.550
.525
.500
.475
.450
TEMPERATURE-°F
100
200
300
400
500
600
700
800
900
1000
300#
250
225
200
175
150
125
100
90
80
70
60
50
40
30
25
20
15
10
5
3
1#